Density, Viscosity and Solubility of Carbon Dioxide in Aqueous Blends of Diethanolamine and 2-Amino-2-Hydroxymethyl-1, 3-Propanediol

by

Ting Sing Tat

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2012

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CERTIFICATION OF APPROVAL

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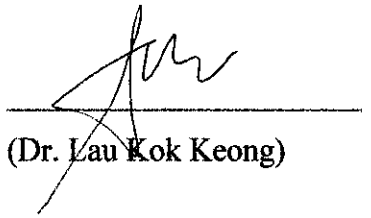
Approved by,



(Dr. Lau Kok Keong)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

TING SING TAT

ABSTRACT

In this study, solubility of carbon dioxide (CO_2) in new aqueous blends of diethanolamine (DEA) + 2-amino-2-hydroxymethyl-1, 3-propanediol (AHPD) was carried out at temperatures of (303 K and 333 K) and CO_2 partial pressure ranging from (100 – 2000 kPa). The total aqueous blends amine mass fraction was kept within 30 wt% in all solutions, varies at (30 wt% DEA + 0 wt% AHPD), (20 wt% DEA + 10 wt% AHPD), (10 wt% DEA + 20 wt% AHPD) and (0 wt% DEA + 30 wt% AHPD). The results show higher CO_2 loading capacity is achieved when the system is operated at lower temperature and at higher CO_2 partial pressure. At a fixed temperature, an increase in mass fraction of AHPD in the aqueous blends solution leads to higher CO_2 loading capacity. CO_2 loading capacity was found highest in the blends of 10 wt% DEA + 20 wt% AHPD at 1680 kPa and 303 K, which is 1.2814 mol of CO_2/ mol of absorbent. Physical properties such as density and viscosity of DEA + AHPD are also measured at temperature of (303 K - 333 K).

ACKNOWLEDGEMENT

This page is dedicated to all who have contributed to the success of my final year project on the topic of "Density, Viscosity and Solubility of Carbon Dioxide in Aqueous Blends of Diethanolamine and 2-Amino-2-Hydroxymethyl-1, 3-Propanediol".

First and foremost, thanks would like to be given to project supervisor, Dr Lau Kok Keong, who has guided and give financially support throughout the entire project. All the equipments and chemicals are provided to ensure the project can be started on time. His contribution is indeed precious.

My deepest gratitude also goes to Mr. Murshid, who is a postgraduate student from Universiti Teknologi PETRONAS. He has provided good guidance and demonstration on equipments operation. Undeniably, his support has ensured my project flow went smoothly.

Lastly, thousand of thanks go to Universiti Teknologi PETRONAS, which provides me a proper place to perform laboratory work. Not to forget also Mr. Mohd Shahafizan bin Zulkifi, the technician of the laboratory, who assists and give advices on handling the chemicals and equipments. Thanks.

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INTRODUCTION

1.1 PROJECT BACKGROUND

In the past few decades, removal of CO_2 has become one of the most important environment issues when CO_2 is the major greenhouses gases that emitted from combustion of fossil fuel. The increasing CO_2 emission and global warming have challenged the world scientists to think critically for a better solution to mitigate the problem while meeting the need of energy for the world.

Above mentioned are all environmentally-related issues, but from industrial point of view, the presence of CO_2 in the process stream give impacts on the plant operation as well. For instant, failing to remove acid gases can lead to corrosion of pipes and the other processing equipment. Existence of CO_2 in the process stream could also affect on the heating value, commercial value and purity of the commercial products such as natural gas.

This has also motivated the researches to study extensively on CO_2 capture where new and more energy-efficient absorbents or solvents should be invented. The removal of acid gas by absorption using reactive solvent has been the most commonly method used in industries although there are other methods available such as membrane separation and physical or chemical adsorption. A wide variety of alkanolamines are applied for CO_2 absorption in the gas and chemical industries starting from monoethanolamine (MEA), diethanolamine (DEA), N-methylehtanolamine (MDEA) and diisopropanolamine (DIPA), followed by the new discovery of new class of amine, sterically hindered amines for instance, 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), 2-piperidineethanol (2-PE) and others. Recently, researchers figure out that by mixing different alkanolamines, the new mixed solution can combine strong features of the constituent amines. The mixed amine

systems, which combine the higher equilibrium capacity of tertiary amines with the higher reaction rate of primary or secondary amines, can enhance the absorption rate and has great saving in the solvent regeneration energy.

1.2 PROBLEM STATEMENT

Today, DEA is used as the solvent for CO_2 removal at most of the gas treating field. DEA is found not only lead to ***high solvent regeneration cost*** but also has relatively ***low CO_2 loading*** (limited to 0.5 mol CO_2/mol amine). Hence, new solvent should be discovered to improvise the CO_2 loading capacity.

In this project, DEA is mixed with AHPD with the aim to improve the CO_2 loading capacity instead of using DEA alone as solvent. Blended amine is chosen as the method to improve the solvent performance because it is the combination of a fast reactivity from a primary or secondary amines coupled with high absorption capacity and low regeneration cost from a tertiary or sterically hindered amines. Hence, study is carried out on the solubility of CO_2 and the physical properties of aqueous blends of DEA + AHPD such as density and viscosity.

Information on blends of AMP with primary and secondary amines is available in the literature such as Hong (1996), Bandyopadhyay (2003, 2004, and 2005) and Kundu (2012). ***However, the physicochemical properties of aqueous blends of DEA with AHPD have not been reported in the open literature so far***. Hence, it is significant to carry out this study as the proposed blends solution could be a potential solvent in industrial application.

1.3 OBJECTIVE

- To enhance CO_2 loading capacity of DEA by blending it with AHPD
- To measure the solubility of CO_2 and physical properties of the aqueous blends amine (DEA + AHPD) such as density and viscosity

1.4 SCOPE OF STUDY

In this project, the total aqueous blends amine mass fraction in all solutions was kept within 30% in view of recent interest in using concentrated amine solution in gas treating (Paul and Mandal, 2006). Temperature and pressure are two very important parameters to determine the CO_2 solubility into the solution. Hence, solubility of CO_2 was measured from temperature and CO_2 partial pressure ranging from 303 K- 333 K and 100 - 2000 kPa respectively to study on the effects of these parameters. Four difference mass fractions of the aqueous solutions will be used as solvent to study on the effect of mass fraction of alkanolamines to the CO_2 solubility. On top of that, solubility data will be compared to prove that aqueous blends amine solution is better than single amine solution. Upon completion of experimental work, data will be analyzed to choose the optimum condition for this blends amine solution in CO_2 capture.

Knowledge of physical properties such as density and viscosity is essential for the process design of equipments for process using these solvents. For instance, when designing a CO_2 absorber column's diameter, density is needed and the formula is as follows (Douglas, 1988):

$$D_T = 0.0164\sqrt{V}\left(\frac{M_G}{\rho}\right)^{1/4}$$

Douglas (1988) also mention even for a simple case of a double-pipe heat exchanger, one of the variables required is viscosities of fluid mixture on both the tube and shell sides of the exchanger. One of the equations in designing heat exchanger is as follow:

$$\frac{h_i}{k} = 0.023\left(\frac{DG}{\mu}\right)^{0.8}\left(\frac{C_p\mu}{k}\right)^{\frac{1}{3}}\left(\frac{\mu}{\mu_w}\right)^{0.14}$$

Besides, these properties are important in the mass transfer rate modeling of absorption and regeneration because they affect the liquid-film coefficient for mass transfer.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION OF ALKANOLAMINES

Alkanolamines are the chemical compounds that have at least one hydroxyl group and one amino group. Hydroxyl group helps to reduce the vapor pressure and hence increase the solution solubility while amino group that is alkaline, promotes the reaction with acid gases such as CO_2 and H_2S. The reaction between alkanolamines and CO_2 is exothermic and reversible reaction.

Class of alkanolamines can be differentiated by the number of substitution on the central nitrogen atom; a single substitution is named as primary amine, double substitution is secondary amine and triple substitution is tertiary amine. Alkanolamines from these three classes are widely used in the gas treating industrial to capture CO_2 and H_2S. MEA (primary amine) and DEA (secondary amine) are often used to remove CO_2 and H_2S totally from sour natural gas and industrial gas streams, while on the other hands, aqueous MDEA (tertiary amine) selectively remove H_2S from gas streams that containing both CO_2 and H_2S. (Bandyopadhyay, 2005).

Sterically hindered amine can be defined as an amine with a primary or secondary amine in which attached to one or more central carbon atoms linked to nitrogen atom. For example, AMP is the hindered form of MEA where its two hydrogen atoms attached to carbon atom is substituted by two methyl groups. (Iluita, 2012). These substitutions that form bulky group adjacent to amino group will determine the properties of sterically hindered amines such as absorption capacity, regeneration efficiency, reactivity and others.

The interest in the use of mixed amine solvents in gas-treating process is increasing. Chakaravarty (1985) reported that the application of blended amines enhanced the absorption capacity and absorption rate compared to a single amine solvent. From economic point of view, solvent circulation rate is a major consideration in the gas treating industries that use chemical solvents. Blends amine offers lower solvent circulation rate due to the higher CO_2 equilibrium capacity. Furthermore, selectivity of blended amine solvent to remove acid gas can be varied by changing the concentration of the constituent amines in the blend. (Bandyopadhyay 2005). There are some blends amines have been suggested for the industrial gas-treating process, for instance mixtures of MEA and MDEA or DEA and MDEA (Chakaravarty, 1985; Kohl, 1997; Bandyopadhyay 2006).

The characteristic of each class of amine is summarized as table below:

Table 1: Characteristic of Each Class of Amine

	CO_2 Absorbents			
	MEA or DEA	**MDEA**	**Sterically Hindered Amine**	**Mixed Amine**
Reaction Rate	High	Low	High	High
Regeneration Cost	High	Low	Low	Low
CO_2 Loading	0.5 mol CO_2/mole amine	0.5 mol CO_2/mole amine	1.0 mol CO_2/mole amine	1.0 mol CO_2/mole amine
Source	(Satori, 1983) (Iliuta, 2005)	(Hong, 1996) (Iliuta, 2010)	(Satori, 1983) (Bandyopadhyay, 1995)	(Chakravarty, 1985)

2. 2 MECHANISM OF REACTION BETWEEN ALKANOLAMINES AND CO_2

Reactions between alkanolamines and CO_2 differ at each class of alkanolamines. In next section, the detail explanations will be given on the reactions that occur which lead to difference performances in different classes of amine as mentioned in Table 1.

2.2.1 Primary (RNH_2) and Secondary (R_2NH) Amines

There are two mechanisms for reaction between CO_2 and amines. First is zwitterions mechanism as proposed by Caplow (1968) and Danckwerts (1979). In this mechanism, zwitterions will form as intermediate in the solution. Then, the proton from the zwitterions will react with base (B) such as amine. The reaction is as below:

Formation of carbamate, $RNHCOO^-$ and protonated amine, RNH_3^+

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^-$$

$$RN^+H_2COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$

Global reaction:

$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$

Second mechanism is termolecular mechanism as proposed by Crooks and Donnellan (1989). In this reaction, only one step is involved. The reaction is as below:

$$CO_2 + RNH_2 + B \leftrightarrow RNHCOO^- + BH^+$$

With regards to the formation of stable carbamates, primary and secondary alkanolamines such as MEA and DEA are well known with fast reactivity. However, Iluita (2012) points out the stable carbamates are difficult to be reverted to fresh amine. This eventually will lead to longer regeneration time and more energy consumption. On the other hands, (Satori and Savage, 1983) and (Iliuta, 2010) agree that due to the carbamtes formation, primary and secondary amines have relatively low absorption which only limited to 0.5 mol CO_2/mol amine.

2.2.2 Tertiary (R_3N) Amines

Tertiary amine has no hydrogen atom attached to nitrogen atom, unlike primary and secondary amine, CO_2 reaction can only occur after CO_2 dissolves in water. (Zare,

2009). Hence it has more tendencies to undergo hydrolysis reaction to form bicarbonate ion. The reaction is as below:

Bicarbonate (HCO_3^-) formation

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

Amine protonation

$$R_3N + H^+ \leftrightarrow R_3NH^+$$

Global reaction:

$$R_3N + CO_2 + H_2O \leftrightarrow R_3NH^+ + HCO_3^-$$

Iluita (2010) reported that these bicarbonate undertake desorption process at higher rate and upshot in less energy consumption at regeneration column. Besides, Vaida (2009) mentioned that bicarbonate reaction is less exothermic than carbamate reaction. Thus, it results in lower solvent regeneration cost. Characteristic of tertiary amine, in short, able to reduce the main operational cost of gas treating process as the stripping unit is highly energy consuming. (Iluita, 2010). On the drawback side, from Subhasish's report, it stated that bicarbonate reaction is relatively slow. Therefore, slow reaction with CO_2 limits the use of MDEA. (Hong, 1996).

2.2.3 Sterically Hindered Amines

There are three simultaneous mechanisms for the reaction between sterically hindered amines and CO_2.

(i) Same Bicarbonate formation mechanism with tertiary amines

(ii) Bicarbonate formation by zwitterions hydrolysis

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^-$$

$$RNH_2^+COO^- + H_2O \leftrightarrow RNH_3^+ + HCO_3^-$$

Global reaction:

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^-$$

(iii) Bicarbonate formation by carbamate hydrolysis

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^-$$
$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$
$$RNHCOO^- + H_2O + (RNH_3^+) \leftrightarrow RNH_2 + (RNH_3^+) + HCO_3^-$$

Global reaction:

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^-$$

Due to the hindrance of the bulky group in sterically hindered amines, unstable carbamate ions are formed in the reaction with CO_2 through hydrolysis. This will then releasing free amine to react with CO_2 again which give significantly higher loading capacity of 1 mol of CO_2 per mole of amine. (Bandyopadhyay 2003 and Mandal 2009). There is growing interest in using sterically hindered amine to capture CO_2 as it offers higher absorption capacity, higher absorption rate, and degradation resistance advantages over the conventional alkanolamines. On top of that, it is expected that a solution contains more bicarbonates are easier to be stripped off from CO_2 and produces lean solution. (Sartori and Savege 1983).

2.3 SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS MIXTURE

Three parameters that affect solubility of carbon dioxide in aqueous mixture are: pressure, temperature and the aqueous mixture composition.

2.3.1 Effect of Pressure on CO_2 Solubility

Solubility of gas favors in high pressure system. When the system is at equilibrium state, rate of gas molecules enter the solution equivalent to the rate of solutes escape from the solution. Referring to the diagram illustrated in Figure 1(b), when pressure is applied to the system and compresses the gas above the solution, more gas molecules present in the

solution as the rate of gas molecules enter the solution increase. In addition, Henry's Law states that solubility of gases in solution is directly proportional to the pressure of the gas above the surface of the solution. This can be expressed as:

$$C = k * P_{gas}, \textit{ where}$$

C = the solubility of gas in solvent

k = the proportionality constant

P_{gas}= the partial pressure of the gas above the solvent

Thus, the solubility of gas increases as the partial pressure above the solution increases.

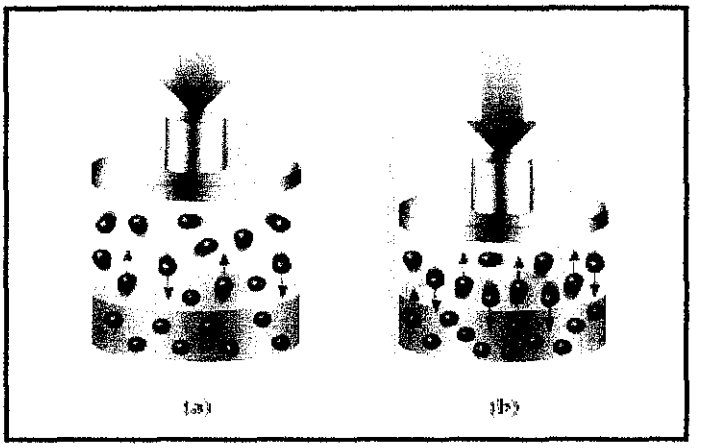


Figure 1: Effect of Pressure on the Solubility of a gas.
(Source: http://wps.prenhall.com/wps/media/objects/3312/3391718/blb1303.html)

2.3.2 Effect of Temperature on CO_2 Solubility

For gas phase, CO_2 solubility decreases when the temperature of the solution increases. Increase of temperature allows the gases (CO_2) to gain more kinetic energy and hence it can move freely. In second law of thermodynamic stated that heating of solution shifts gases to disorder state and they are highly disperse. On top of that, at higher temperature, molecules of the solvent will tend to break their intermolecular bonds and escape from the solution. Therefore, less CO_2 exist in the solution when the temperature of the solution is high or in other words, less CO_2 has been captured. As the reaction is exothermic, when the temperature is elevated, the equilibrium tends to shift to the left according to Le Chatelier's principle. Hence, less CO_2 is absorbed.

2.3.3 Effect of Aqueous Mixture Solution (Solvent) Composition on CO_2 Solubility

Since single amine solvent has its limitation such as low CO_2 loading capacity for primary or secondary amine and slow absorption rate for tertiary amine, use of mixed amine solvents can be another alternative to overcome the limitations. Mixed amine solvent is the combination of higher reaction rate of the primary or secondary amines and higher CO_2 loading capacity from tertiary amines or sterically hindered amines. Therefore, according to Chakaravarty (1985), the application of blended amines can enhance the absorption rate and great saving in the solvent regeneration energy.

In this project, AHPD from sterically hindered amine class is blended with DEA from secondary amine class, with the aim to improve CO_2 loading capacity and the absorption rate. AHPD is chosen due to its characteristic of low stability constants and easily undergo hydrolysis process that can release free amine. When more CO_2 is able to react with this free amine, an overall stoichiometric loading capacity will become 1 mol of CO_2/ mol of amine with appreciable rate of absorption (Sartori and Savage, 1983). Hence, increase mass fraction of AHPD in the mixed aqueous solution will help to increase CO_2 loading capacity.

Summary: From the study of the literatures, loading capacity decreases with increases of temperature; the loading capacity increases with increases of pressure; loading capacity increases with increases of tertiary amine or sterically hindered amines concentration. The statement was reported by Hong (1996), Murgesan (2009) and Kundu (2012) in their works. Solubility of CO_2 in (DEA + AMP) has been reported both by Hong (1996) and Kundu (2012). Comparing at the same parameters such as temperature, both results show good agreement that the CO_2 loading capacity decreases with increasing temperature. The results for the CO_2 solubility in this study are reported by measuring the moles of CO_2 per moles of alkanolamine in the solution.

2.4 DENSITY AND VISCOSITY OF AQUEOUS MIXUTURE

Bandyopadhyay (2003) have measured the density and viscosity of aqueous blends solutions where MDEA and AMP are the tertiary amines combine with primary amine, MEA and secondary amine, DEA over the temperature range of 298 K to 333 K. Density of aqueous blends amines (MDEA and MEA/DEA) is higher than (AMP and MEA/DEA). These aqueous blends amines have the similar trend that the density is decreasing when the temperature is increasing and the composition of tertiary amine is decreasing. On the other hand, (MDEA and MEA/DEA)'s viscosity is lower than (AMP and MEA/DEA). However, viscosities of these blend aqueous amines are decreasing at higher temperature and at lower composition of tertiary amine. The correlated densities and viscosities of the ternary mixtures are in excellent agreement with the experimental data over the temperature and relative composition ranges studied.

Mandal (2006) has also done the similar work by using the aqueous blends solutions (2-PE + MEA/DEA) from 288 K to 333 K. The work differs from others in the way that the density of the mixtures decreases with the increasing composition of 2-PE in the mixture.

Bandyopadhyay (2006) and Murshid (2011) have published the physical properties for aqueous solutions of (AMP + PZ) and (AHPD + PZ) respectively at 298 K to 333 K. From Bandyopadhyay (2006)'s study, the density decreases linearly with the increasing temperature and increases as the PZ concentrations increases in the aqueous AHPD. The viscosity values show a nonlinear decreasing trend while increasing the temperature. However, the values increase with the increase of PZ concentration in aqueous AHPD. Same trends were observed from the Murshid (2011)'s study.

2.5 CO_2 LOADING CALCULATION METHOD

In Abdi (2005)'s work, he has presented the method to calculate CO_2 loading and in this study, CO_2 loading was calculated using the same method.

Step 1: Mole of CO_2 feed,

$$n_{co_2} = \frac{V_{MV}}{RT_a}\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right)$$

where V_{MV} = volume of mixing vessel

Z_1 and Z_2 = the compressibility factors corresponding to the pressure

P_1 and P_2 = initial pressure and final pressure respectively before and after transferring CO_2

T_a = ambient temperature

Step 2: Moles of CO_2 in gas phase,

$$n_{co_2} = \frac{V_{EC} P_{CO_2}}{Z_{CO2} RT}$$

where V_{EC} = volume of equilibrium cell

Z_{CO2} = the compressibility factor corresponding to partial pressure of CO_2

P_{CO2} = partial pressure of CO_2 (pressure after the system reaches equilibrium)

T = temperature of equilibrium cell

Step 3: Mole of CO_2 in liquid phase = Mole of CO_2 feed – mole of CO_2 in gas phase

Step 4: CO_2 loading in liquid phase, $\alpha = n_{CO2}/n_{amine}$

Where n_{CO2} = the mole of CO_2 in liquid phase

n_{amine} = the moles of amine in liquid phase = $n_{amine} = \frac{m_{amine}\rho V_1}{M_{amine}}$

m_{DEA} = mass fraction of amine in the aqueous solution

ρ = aqueous solution density

V_1 = the volume of amine in the cell

M_{amine} = molecular weight of amine

CHAPTER 3
METHODOLOGY

3.1 CHEMICAL SOLUBILITY EXPERIMENT

The CO_2 solubility measurement setup used in this study is similar to the one reported in Thanapalan's (2009) work. The schematic diagram of the setup is shown in Figure 2. Initially, the desired temperature of equilibrium cell (volume of 0.1 L) was set and maintained by PROTECH Digital Heating Circulators HC-10 with accuracy of temperature measurement ± 0.1 °C. To remove all the possible moistures trapped inside the setup, the system was purged by nitrogen for 5 minutes. Mixing vessel (volume of 3 L) was then pressurized with CO_2 until the desired pressure. While waiting for the pressure to be stabilized, approximately 10 mL of aqueous blends solultion was pumped into the equilibrium cell by metering pump. The equilibrium cell was vacuumed up to approximately 26 kPa before being fed with the solvents. Then, CO_2 was transferred to equilibrium cell and stirrer helps to enhance the contact between CO_2 and the blends. When the pressure of equilibrium cell was observed to remain constant, it was assumed that the system has reached the equilibrium state. The time required for the system to achieve equilibrium was depending on the pressure applied to the system, which approximately ranging from 2 hours till 12 hours.

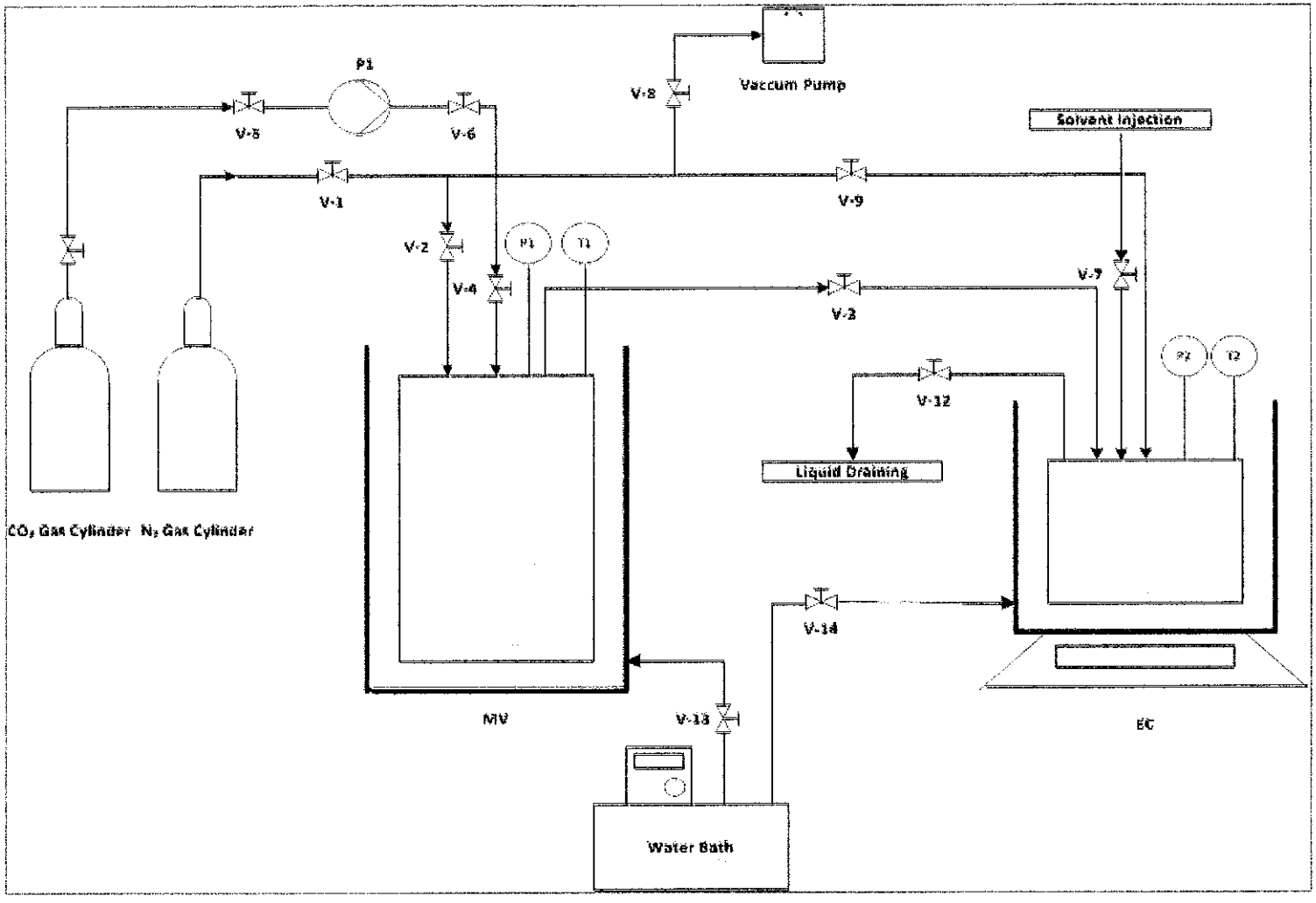


Figure 2: Schematic diagram of SOLTEQ BP-22 high pressure solubility cell.

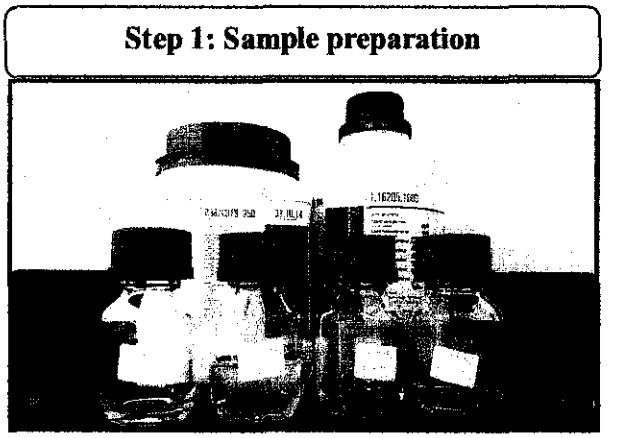


Figure 3: 99.5% purity of DEA and 99.8% purity of AHPD from Merck, Malaysia

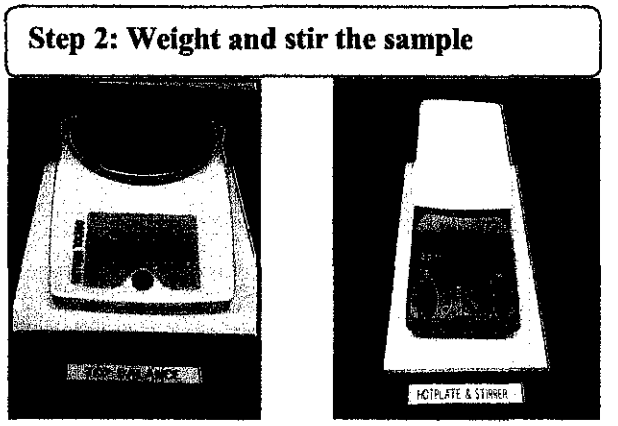


Figure 4: Mettler Toledo- Top Balance (left) and Curning PC-420D- Hot Plate and Stirrer (right)

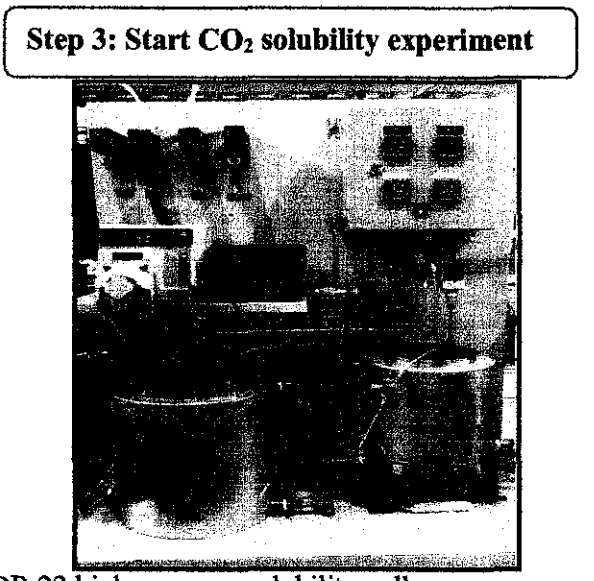


Figure 5: SOLTEQ BP-22 high pressure solubility cell

3.2 DENSITY

Densities of aqueous blends solutions DEA + AHPD were measured at the temperature vary from 303 K to 333 K at atmospheric pressure. The solutions were fed in a U-shaped borosilicate glass tube embedded in the density meter (Anton Paar, DMA 4500 M) and were being excited to vibrate. Densities were measured depending on the samples characteristic frequency.

$$Density = KA \times Q^2 \times f_1 - KB \times f_2$$

where KA and KB is apparatus constant, Q is the quotient of the period of oscillation of the U-tube divided by the period of the oscillation of the reference oscillator and f_1 and f_2 is the correlation terms for the temperature, viscosity and nonlinearlity. The allowable errors in the measurement of densities were approximately 1 x 10^{-5} g/cm^3 and for temperature were ± 0.01 K.

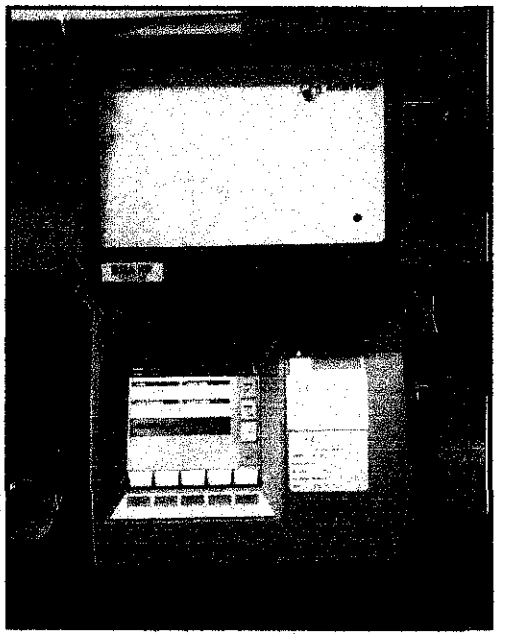


Figure 6: Anton Paar Density Meter: DMA 4500 M

3.3 VISCOSITY

Viscosities of aqueous blends solutions DEA + AHPD were measured at the temperature vary from 303 K to 333 K at atmospheric pressure using microviscometer (Anton Paar, Lovis 2000 M/ME). A capillary which filled with the solutions and a ball, were inserted in the rotating capillary block. The runtime of the ball rolling inside the capillary is proportional to viscosity.

$$\eta = K.(\rho_b - \rho_s).\Delta t$$

where η is dynamic viscosity, K is the constant of proportionality, ρ_b and ρ_s is ball density and sample density respectively and Δt is the rolling time. The accuracy of the viscosity and temperature measurements were up to ±0.5% and ±0.02 K respectively.

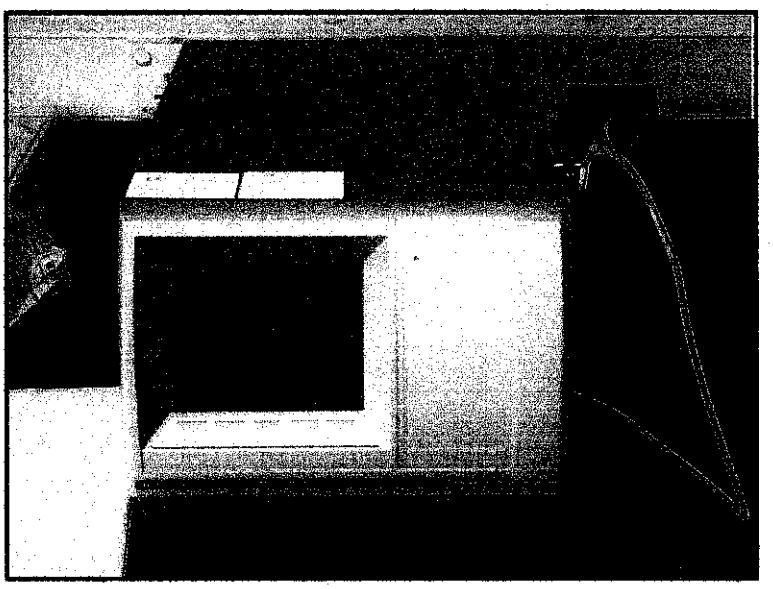
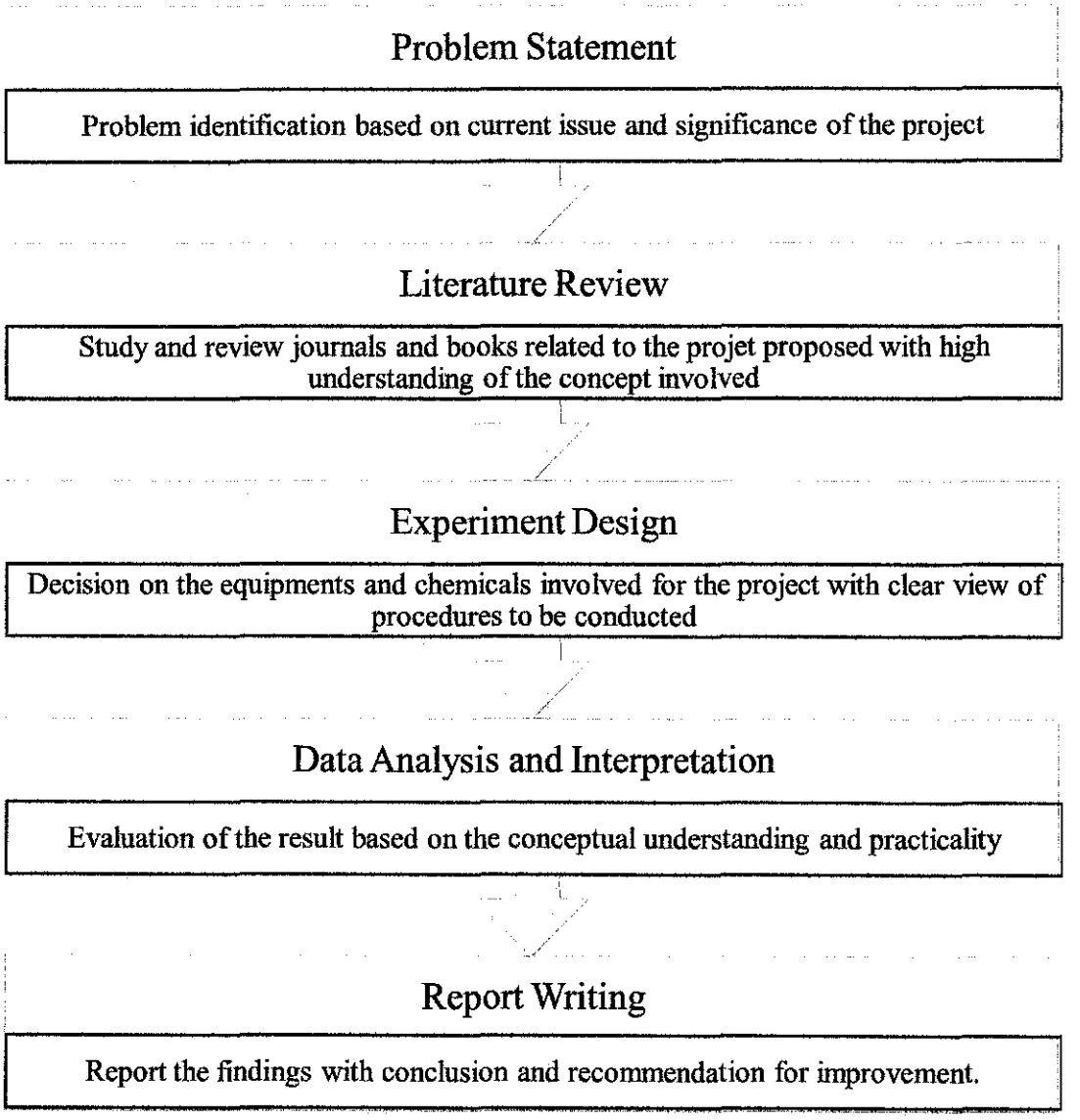


Figure 7: Anton Paar Microviscometer: Lovis 2000 M/ME

3.4 RESEARCH METHODOLOGY



3.5 KEY MILESTONE

No	Action Item	Note
1.	Perform Laboratory Work	Done
2.	Submission of Progress Report	Assessment Form 07
3.	Pre-EDX	Assessment Form 08
4.	Submission of Soft Copy Dissertation	Assessment Form 10
5.	Oral Presentation	Assessment Form 09
6.	Submission of Technical Paper	To be submitted

3.6 GANTT CHART

NO.	ACTIVITY / WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Perform Laboratory Work														
2.	Submission of Progress Report														
3.	Pre-EDX														
4.	Submission of Soft Copy Dissertation														
5.	Submission of Technical Paper														
6.	Oral Presentation (To be announced)														

Figure 8: Gantt Chart

CHAPTER 4
RESULTS AND DISCUSSION

4.1 EXPERIMENTAL DATA FOR CO_2 SOLUBILITY

Solubility of CO_2 in aqueous solution of DEA + AHPD at 303 K and 333 K, from CO_2 partial pressure ranging from 100 kPa till 2000 kPa is measured and tabulated in Table 2. The concentration of alkanolamine aqueous solution varies at (30 mass% DEA + 0 mass% AHPD), (20 mass% DEA + 10 mass% AHPD), (10 mass% DEA + 20 mass% AHPD) and (0 mass% DEA + 30 mass% AHPD).

Table 2: Solubility of CO_2 in DEA + AHPD Aqueous Solution at 303 K and 333 K

DEA + AHPD mass fraction	T= 303 K		T= 333 K	
	P_{CO2}/kPa	α	P_{CO2}/kPa	α
30 + 0	245	0.7087	241	0.6241
	824	0.7834	736	0.6963
	1265	1.1151	1197	0.9858
	1678	1.2069	1714	1.1767
20 + 10	265	0.6154	318	0.5442
	723	0.8794	855	0.7460
	1158	1.1748	1167	1.0909
	1658	1.2387	1736	1.2008
10 + 20	287	0.6529	330	0.5904
	638	1.0268	733	0.8614
	1126	1.2038	1143	1.1196
	1680	1.2814	1635	1.2508
0 + 30	287	0.6684	356	0.6117
	667	1.0618	751	0.9530
	1127	1.2559	1204	1.1628
	1655	1.3259	1635	1.2958

4.1.1 Effect of Temperature and CO_2 Partial Pressure on CO_2 Loading

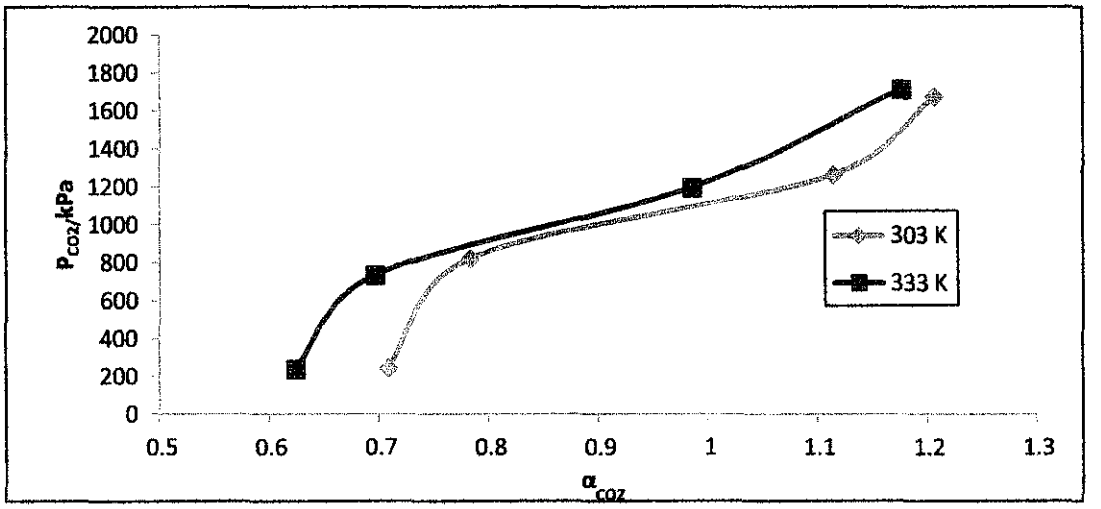


Figure 9: Solubility of CO_2 in aqueous solution of 30 wt% DEA+ 0 wt % AHPD at T = 303 K and 333 K

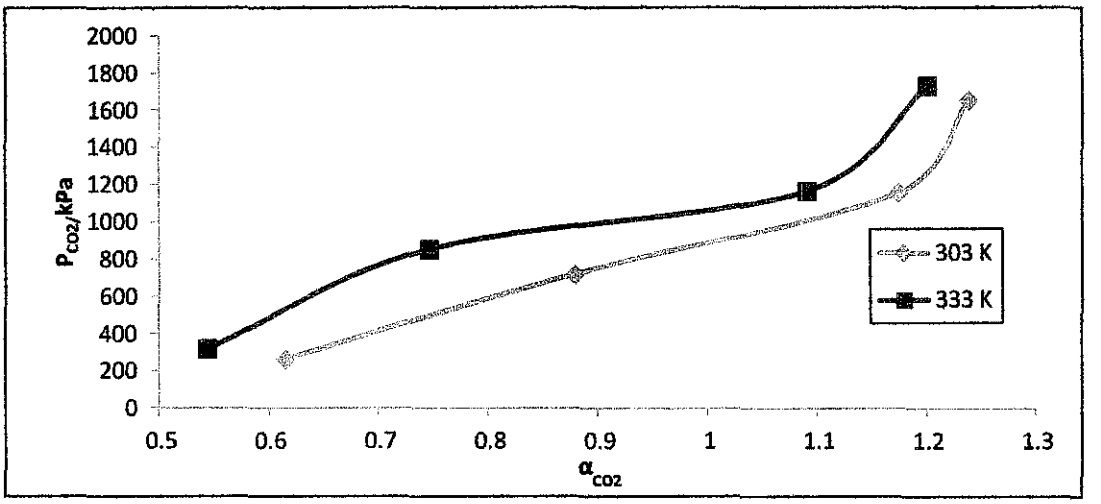


Figure 10: Solubility of CO_2 in aqueous solution of 20 wt% DEA+ 10 wt % AHPD at T = 303 K and 333 K

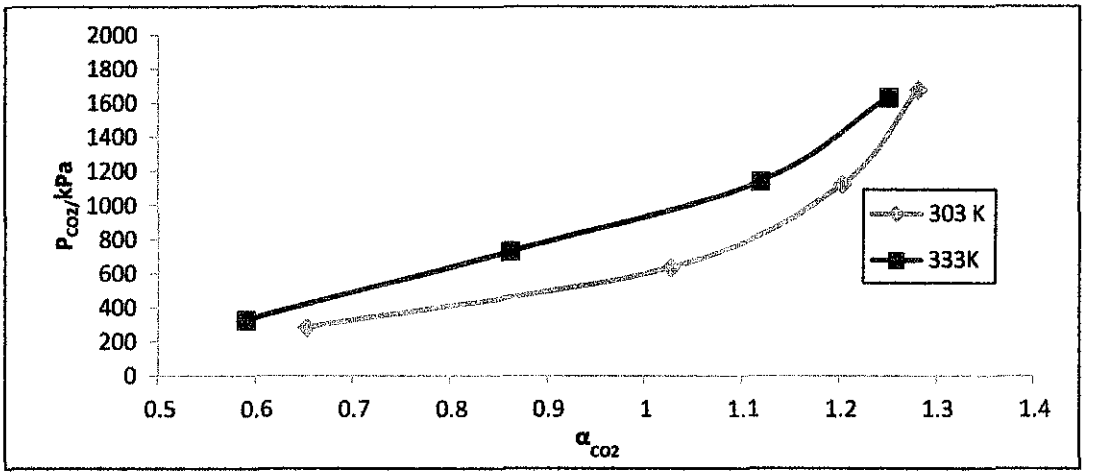


Figure 11: Solubility of CO_2 in aqueous solution of 10 wt% DEA+ 20 wt % AHPD at T = 303 K and 333K

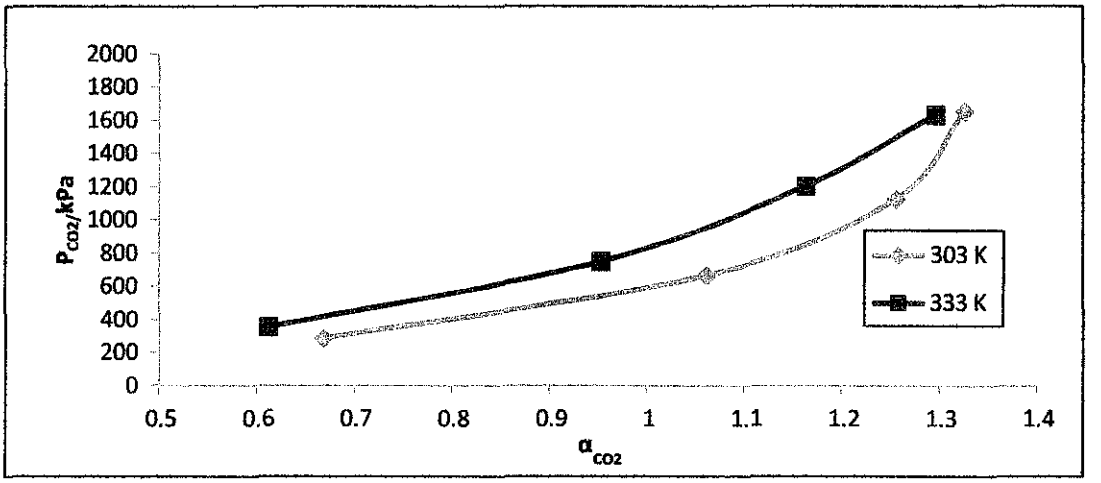


Figure 12: Solubility of CO_2 in aqueous solution of 0 wt% DEA+ 30 wt % AHPD at T = 303 K and 333K

Graphs of CO_2 partial pressure as the function of CO_2 loading at fixed concentration are presented in Figure 9 - 12. From Figure 9 - 12, it can be observed that higher CO_2 loading capacity is achieved when the system is operated at lower temperature. On the other hand, higher CO_2 loading capacity can be obtained at higher CO_2 partial pressure. Hence, temperature and CO_2 partial pressure are the parameters that should be taken into consideration during gas treating process.

4.1.2 Effect of Concentration on CO_2 Loading

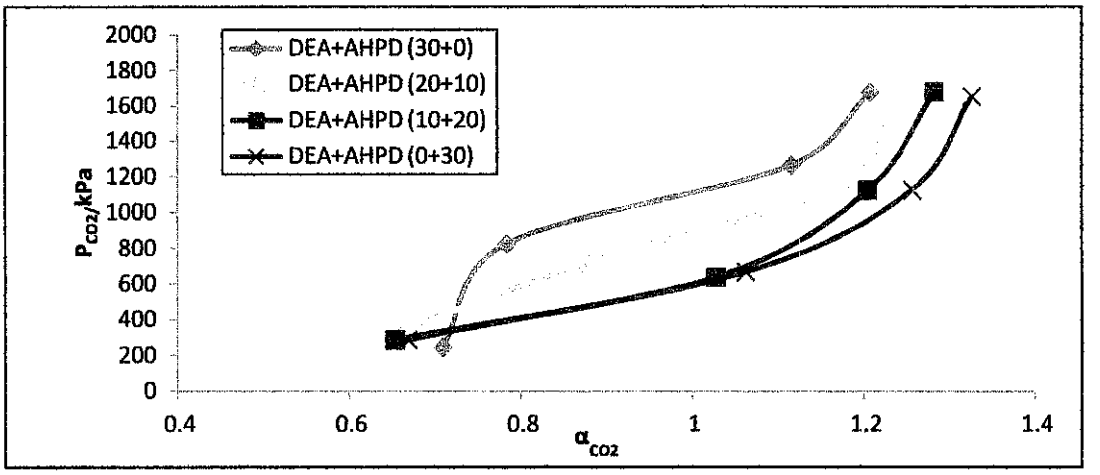


Figure 13: Solubility of CO_2 in different concentration of aqueous solution at T = 303 K

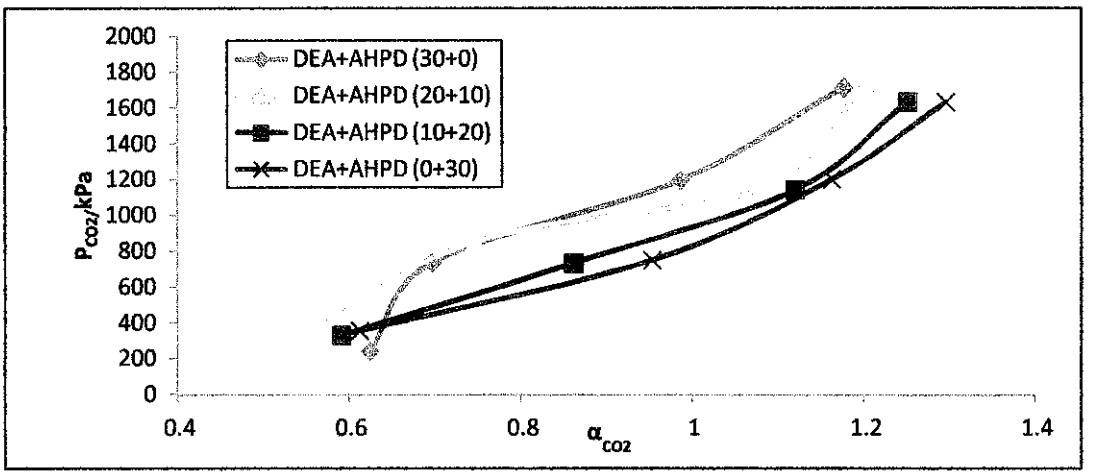


Figure 14: Solubility of CO_2 in different concentration of aqueous solution at T = 333 K

To study on the effect of different amine concentration to CO_2 solubility, plot of CO_2 partial pressure as the function of CO_2 loading in four different amine concentrations at fixed temperature are illustrated in Figure 13 and 14.

From Figure 13 and 14, at low partial pressure up to 400 kPa at 303 K and 600 kPa at 333 K, aqueous DEA solutions has higher CO_2 loading compared to the aqueous blends

solution, however, become lower at higher partial pressure. This trend was also observed at other mixed solvent experimental data such as AMP + TMS as reported by Roberts and Mather (1988) and MEA + MDEA and DEA + MDEA in Meisen's work (1994).

Apart from that, it is also observed from the graphs that aqueous AHPD solution is performing better in absorbing CO_2 as compared to aqueous DEA solution at CO_2 partial pressure more than 400 kPa at both 303 K and 333 K. Therefore, by blending DEA with AHPD, CO_2 loading capacity is expected to increase. This statement agrees well with the result obtained in this work. It is the evidence from the Figure 13 and 14 that at a fixed temperature, an increase in mass fraction of AHPD in the aqueous blends solution brings to higher CO_2 loading capacity.

4.2 DENSITY

Density measurements data for different concentration of aqueous blends solution of DEA and AHPD for the temperature range (303 K - 333 K) is presented in Table 3. Experimental data obtained from this study on densities of 30 wt% DEA aqueous solution were compared with the data reported by Bandyopadyay (2003) and Li (1997) for validation. The comparison data is presented in Table 4.

Table 3: Density of DEA + AHPD Aqueous Solution from T = 303 K to 333 K

DEA + AHPD	ρ/g.cm^{-3}						
mass%/mass%	303 K	308 K	313 K	318 K	323 K	328 K	333 K
30/0	1.03083	1.02864	1.02630	1.02383	1.02126	1.01856	1.01577
10/20	1.05883	1.05666	1.05436	1.05192	1.04932	1.04653	1.04347
20/10	1.04460	1.04229	1.03998	1.03754	1.03498	1.03230	1.02949
0/30	1.07445	1.07227	1.06993	1.0674	1.06482	1.06204	1.05924

Table 4: Comparison of Density of 30 wt% Aqueous DEA Solution Measured in This Work with Literature Values

	ρ/g.cm^{-3}				
	30 wt% DEA			30 wt % DEA	
T/K	Bandyopadyay(2003)	this work	T/K	Li(1997)	this work
303	1.0332	1.03083	303	1.0306	1.03083
308	1.0291	1.02864	313	1.0264	1.02630
313	1.0264	1.02630	323	1.0225	1.02126
318	1.0227	1.02383	333	1.0172	1.01577
323	1.0193	1.02126			
100AAD		0.117[a]			0.074[a]

$$^{a}AAD = \frac{1}{N}\sum_{i=1}^{N}\frac{|\rho_{exp} - \rho_{literature}|}{\rho_{exp}}$$

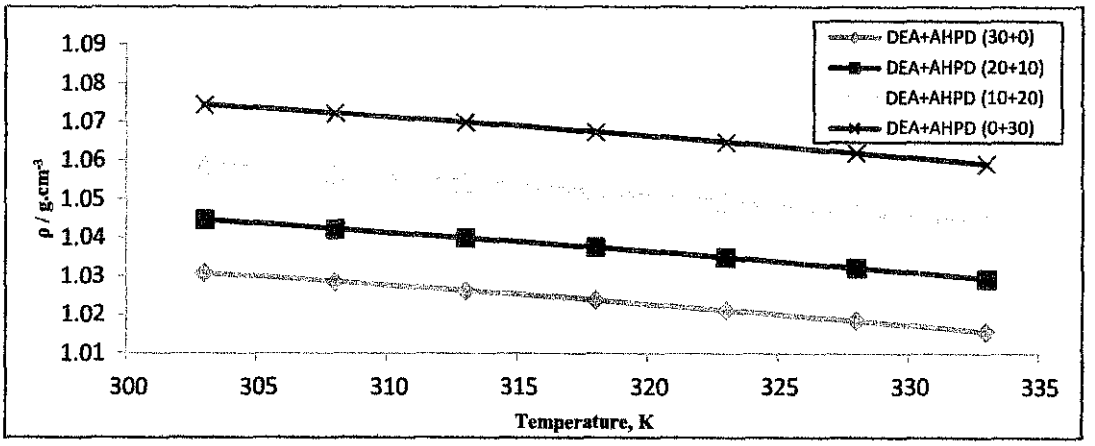


Figure 15: Density of DEA + AHPD at various temperatures

For the density measurements of 30 wt % DEA aqueous solution, the experimental data of this work shows 0.117 % deviation from experimental data of Bandyopadyay at temperatures of (303, 308, 313, 318 and 323) K and 0.074 % deviation from experimental data of Li at temperatures of (303, 313, 323 and 333). Thus, the density data obtained from this study is in good agreement with the literature data. As illustrated in Figure 15, the densities of aqueous blends solution DEA + AHPD decrease with the increasing temperature and decreasing mass fraction of AHPD in the mixture.

4.3 VISCOSITY

Viscosity measurements data for different concentration of aqueous blends solution of DEA and AHPD at the temperature range (303 K - 333 K) is presented in Table 5. Experimental data obtained from this study on viscosities of 30 wt% DEA aqueous solution were measured at temperature range from 303 K to 333 K and compared with the data reported by Li (1997) for validation. The comparison data is presented in Table 6.

Table 5: Viscosity of DEA + AHPD Aqueous Solution from T = 303 K to 333 K.

DEA + AHPD	η/mPa.s						
mass%/mass%	303 K	308 K	313 K	318 K	323 K	328 K	333 K
30/0	2.692	2.329	2.037	1.772	1.575	1.410	1.257
10/20	2.315	2.013	1.765	1.563	1.406	1.264	1.141
20/10	2.439	2.144	1.877	1.655	1.487	1.330	1.210
0/30	2.249	1.976	1.793	1.596	1.417	1.273	1.145

Table 6: Comparison of Viscosity of 30 wt% Aqueous DEA Solution Measured in This Work with Literature Values

	η/mPa.s	
	30 wt% DEA	
T/K	Li (1997)	This work
303	2.542	2.692
313	1.930	2.037
323	1.469	1.575
333	1.218	1.257
AAD		0.044[a]

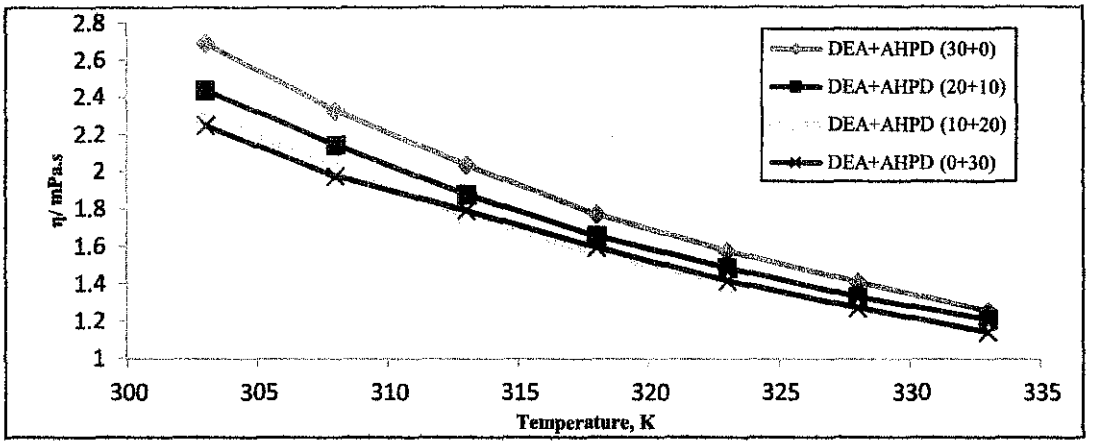


Figure 16: Viscosity of DEA + AHPD at various temperatures

The average absolute deviation of the viscosity measurements for 30 wt % DEA aqueous solution is 0.044. Thus, the viscosity data obtained from this study is in good agreement with the data of Li. As illustrated in Figure 16, the viscosities of aqueous blends solution DEA + AHPD decrease with the increasing temperature and increasing mass fraction of AHPD in the mixture.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

Conclusion: In this study, CO_2 solubility in blend aqueous solution of (DEA + AHPD) was measured at 303 K and 333 K, over the CO_2 partial pressure range from (100 kPa-2000 kPa).

From the result obtained, CO_2 solubility was found dependant on temperature, pressure and mass fraction of DEA and AHPD in the solution. Solubility of CO_2 increases as the CO_2 partial pressure increases but decreases as temperature increases. Besides, CO_2 loading capacity of blend aqueous solution of (DEA + AHPD) is higher compared to using aqueous DEA solution alone as CO_2 capture solvent at high CO_2 partial pressure. CO_2 loading capacity was found highest in the blend of (10 wt% DEA + 20 wt% AHPD) at 1680 kPa and 303 K, which is 1.2814 mol of CO_2/ mol of amine.

Physical properties such as density and viscosity of AHPD+DEA were measured at temperature range of (303 K - 333 K) at atmospheric pressure. These data can be useful for the engineers for their conceptual design phase, for instance in this context is about designing CO_2 absorption column. Both density and viscosity measurements of the aqueous solution agree well with the literature works. Both properties were observed decrease with increasing temperature. However, density of the blends decrease with decreasing mass fraction of AHPD in the mixture, but viscosity of the blends decrease with increasing mass fraction of AHPD in the mixture.

Recommendation: Since CO_2 loading capacity increases by blending DEA with AHPD, this blend aqueous solution has the potential to be recommended to the gas treating industries that are using DEA as absorbent for removal of CO_2. However, more studies should be carried out to investigate on the kinetic of CO_2 absorption and other physical properties such as surface tension and refractive index. The result would be more convincing if the experimental data are compared with other aqueous blend amines.

REFERENCE

Balsora, H. K., & Mondal, M. K. (2011). Solubility of CO2 in an aqueous blend of diethanolamine and trisodium phosphate. *Journal of Chemical & Engineering Data, 56*(12), 4691-4695.

Bougie, F., & Iliuta, M. C. (2010). CO2 absorption into mixed aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol and piperazine. *Industrial & Engineering Chemistry Research, 49*(3), 1150-1159.

Bougie, F., & Iliuta, M. C. (2012). Sterically hindered amine-based absorbents for the removal of CO2 from gas streams. *Journal of Chemical & Engineering Data, 57*(3), 635-669.

Caplow, M. (1968). Kinetics of carbamate formation and breakdown. *Journal of the American Chemical Society, 90*(24), 6795-6803.

Clarke, J. K. A. (1964). Kinetics of absorption of cardon dioxide in monoethanolamine solutions at short contact times. *Industrial & Engineering Chemistry Fundamentals, 3*(3), 239-245.

Crooks, J. E., & Donnellan, J. P. (1989). Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. *Journal of the Chemical Society, Perkin Transactions 2,* (4), 331-333.

Danckwerts, P. V. (1979). The reaction of CO2 with ethanolamines. *Chemical Engineering Science, 34*(4), 443-446.

Dawodu, O. F., & Meisen, A. (1994). Solubility of carbon dioxide in aqueous mixtures of alkanolamines. *Journal of Chemical & Engineering Data, 39*(3), 548-552.

Douglas, J.M. (1988), "Conceptual Design of Chemical Process," *McGraw-Hill*

Harris, F., Kurnia, K. A., Mutalib, M. I., & Thanapalan, M. (2009). Solubilities of carbon dioxide and densities of aqueous sodium glycinate solutions before and after CO2 absorption. *Journal of Chemical & Engineering Data, 54*(1), 144-147.

Hosseini Jenab, M., Abedinzadegan Abdi, M., Najibi, S. H., Vahidi, M., & Matin, N. S. (2005). Solubility of carbon dioxide in aqueous mixtures of N-methyldiethanolamine + piperazine + sulfolane. *Journal of Chemical & Engineering Data, 50*(2), 583-586.

Hsu, C., & Li, M. (1997). Densities of aqueous blended amines. *Journal of Chemical & Engineering Data, 42*(3), 502-507.

Hsu, C., & Li, M. (1997). Viscosities of aqueous blended amines. *Journal of Chemical & Engineering Data, 42*(4), 714-720.

Kumar, G., Mondal, T. K., & Kundu, M. (2012). Solubility of CO2 in aqueous blends of (diethanolamine + 2-amino-2-methyl-1-propanol) and (diethanolamine + N-methyldiethanolamine). *Journal of Chemical & Engineering Data, 57*(3), 670-680.

Kundu, M., & Bandyopadhyay, S. S. (2006). Solubility of CO2 in water + diethanolamine + N-methyldiethanolamine. *Fluid Phase Equilibria, 248*(2), 158-167.

Le Tourneux, D., Iliuta, I., Iliuta, M. C., Fradette, S., & Larachi, F. (2008). Solubility of carbon dioxide in aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol. *Fluid Phase Equilibria, 268*(1–2), 121-129.

Lin, C., Soriano, A. N., & Li, M. (2009). Kinetics study of carbon dioxide absorption into aqueous solutions containing N-methyldiethanolamine + diethanolamine. *Journal of the Taiwan Institute of Chemical Engineers, 40*(4), 403-412.

Mandal, B. P., & Bandyopadhyay, S. S. (2005). Simultaneous absorption of carbon dioxide and hydrogen sulfide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine. *Chemical Engineering Science, 60*(22), 6438-6451.

Mandal, B. P., & Bandyopadhyay, S. S. (2006). Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine. *Chemical Engineering Science, 61*(16), 5440-5447.

Mandal, B. P., Biswas, A. K., & Bandyopadhyay, S. S. (2003). Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine. *Chemical Engineering Science, 58*(18), 4137-4144.

Mandal, B. P., Kundu, M., & Bandyopadhyay, S. S. (2003). Density and viscosity of aqueous solutions of (N-methyldiethanolamine + monoethanolamine), (N-methyldiethanolamine + diethanolamine), (2-amino-2-methyl-1-propanol + monoethanolamine), and (2-amino-2-methyl-1-propanol + diethanolamine). *Journal of Chemical & Engineering Data, 48*(3), 703-707.

Mandal, B. P., Kundu, M., & Bandyopadhyay, S. S. (2005). Physical solubility and diffusivity of N2O and CO2 into aqueous solutions of (2-amino-2-methyl-1-propanol + monoethanolamine) and (N-methyldiethanolamine + monoethanolamine). *Journal of Chemical & Engineering Data, 50*(2), 352-358.

Mandal, B. P., Kundu, M., Padhiyar, N. U., & Bandyopadhyay, S. S. (2004). Physical solubility and diffusivity of N2O and CO2 into aqueous solutions of (2-amino-2-methyl-1-propanol + diethanolamine) and (N-methyldiethanolamine + diethanolamine). *Journal of Chemical & Engineering Data, 49*(2), 264-270.

Mondal, M. K. (2009). Solubility of carbon dioxide in an aqueous blend of diethanolamine and piperazineâ€ . *Journal of Chemical & Engineering Data, 54*(9), 2381-2385.

Murshid, G., Shariff, A. M., Keong, L. K., & Bustam, M. A. (2011). Physical properties of aqueous solutions of piperazine and (2-amino-2-methyl-1-propanol + piperazine) from (298.15 to 333.15) K. *Journal of Chemical & Engineering Data, 56*(5), 2660-2663.

Park, J., Yoon, S. J., Lee, H., Yoon, J., Shim, J., Lee, J. K., et al. (2002). Density, viscosity, and solubility of CO2 in aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol. *Journal of Chemical & Engineering Data, 47*(4), 970-973.

Park, M. K., & Sandall, O. C. (2001). Solubility of carbon dioxide and nitrous oxide in 50 mass methyldiethanolamine. *Journal of Chemical & Engineering Data, 46*(1), 166-168.

Paul, S., Ghoshal, A. K., & Mandal, B. (2009). Physicochemical properties of aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediolâ€ . *Journal of Chemical & Engineering Data, 54*(2), 444-447.

Paul, S., & Mandal, B. (2006). Density and viscosity of aqueous solutions of (N-methyldiethanolamine + piperazine) and (2-amino-2-methyl-1-propanol + piperazine) from (288 to 333) K. *Journal of Chemical & Engineering Data, 51*(5), 1808-1810.

Roberts, B. E., & Mather, A. E. (1988). Solubility of CO_2 and H_2S in a hindered amine solution. *Chemical Engineering Communications, 64*, 105-111.

Saha, A. K., Bandyopadhyay, S. S., & Biswas, A. K. (1993). Solubility and diffusivity of nitrous oxide and carbon dioxide in aqueous solutions of 2-amino-2-methyl-1-propanol. *Journal of Chemical & Engineering Data, 38*(1), 78-82.

Sakwattanapong, R., Aroonwilas, A., & Veawab, A. (2006). Kinetics of CO2 capture by blended MEA-AMP. *EIC Climate Change Technology, 2006 IEEE*, pp. 1-6.

Samanta, A., & Bandyopadhyay, S. S. (2006). Density and viscosity of aqueous solutions of piperazine and (2-amino-2-methyl-1-propanol + piperazine) from 298 to 333 K. *Journal of Chemical & Engineering Data, 51*(2), 467-470.

Seo, D., & Hong, W. (1996). Solubilities of carbon dioxide in aqueous mixtures of diethanolamine and 2-amino-2-methyl-1-propanol. *Journal of Chemical & Engineering Data, 41*(2), 258-260.

Subhasish M. *A Tehcnical Report on Gas Sweetning by Amines.* Report Number 15 , Petrofac Engineering India Ltd.

Vaidya, P. D., & Kenig, E. Y. (2009). CO2 capture by novel amine blends. In Hassan E. Alfadala, G.V. Rex Reklaitis and Mahmoud M. El-HalwagiA - Hassan E. Alfadala,G.V.Rex Reklaitis & Mahmoud M. El-Halwagi (Eds.), *Proceedings of the 1st annual gas processing symposium* (pp. 239-246). Amsterdam: Elsevier.

Zare Aliabad, H., and Mirzaei, S. (2009). Removal of CO2 and H2S using aqueous alkanolamine solusions. *World Academy of Science, Engineering and Technology, 49*

ZHANG, P., SHI, Y., WEI, J., ZHAO, W., & YE, Q. (2008). Regeneration of 2-amino-2-methyl-1-propanol used for carbon dioxide absorption. *Journal of Environmental Sciences, 20*(1), 39-44.

APPENDIX

Table 7: Manual Hand Valves List

Valve No.	Description	Initial Position
V-1	Nitrogen Feed to Mixing Vessel	Close
V-2	Vacuum or Vent for Mixing Vessel	Close
V-3	Gas Feed from Mixing Vessel to Equilibrium Cell	Close
V-4	CO_2 Feed to Mixing Vessel	Close
V-5	Gas Booster P1 Inlet	To bypass
V-6	Gas Booster P2 Outlet	To bypass
V-7	Solvent Feed to Equilibrium Cell	Close
V-8	Vent	Close
V-9	Vacuum or Vent for Equilibrium Cell	Close
V-10	Vent	Close
V-11	N_2O Feed to Mixing Vessel	Close
V-12	Liquid Sampling or Drain from Equilibrium Cell	Close
V-13	Thermostat Inlet to Mixing Vessel Heating Jacket	Close
V-14	Thermostat Inlet to Equilibrium Cell Heating Jacket	Close

CO_2 Solubility Experiment Laboratory Manual

Start Up Procedure

1. Ensure all valves are in initial position. (refer to Appendix, Table 7)
2. Place a beaker beneath and open Valve V-12 to collect any residue in the EC.
3. Open Valve V-2 and V-3 to purge both Mixing Vessel, MV and Equilibrium Cell, EC. Then open Valve V-1 to introduce nitrogen for purging.
4. Wait for 5 minutes until there is no more moisture coming out from Valve V-12.
5. Close valve V-1. Then, close valve V-2, V-3 and V-12 where applicable.

Preparation of CO_2

1. Switch Valve V5 and V6 towards the mixing vessel MV.
2. Enter the CO_2 flow rate at the mass flow controller.
3. Start introducing CO_2 into the MV by opening Valve V4 at the mass flow controller for CO_2 to be used.
4. Immediately open the air drive supply to the gas booster.
5. Allow the CO_2 to pressurize the MV until the desired pressure is reached.
6. Immediately turn off the mass flow controller and close the Valve V4.
7. Close the air drive supply to the gas booster and switch both Valve V5 and V6 towards the bypass line.
8. Allow the pressure in MV to stabilize. Then, record the pressure, P1.

Solubility Experiment

1. Set the desire temperature at thermostat heating bath
2. Open Valve V8 and V9 to create vacuum condition in MV by switch on the vacuum pump. Close Valve V8 and V9 when the pressure in MV is less than atmospheric pressure.
3. Introduce the desired amount of solvent solution using the metering pump through Valve V7.

4. Charge EC with CO_2 from MV by slowly opening Valve V3 until the pressure between both MV and EC are equalized. Close Valve V3.
5. Allow the temperature in EC to stabilize before proceeding.
6. Record P1, T1 and T2.
7. Switch on magnetic stirrer.
8. Monitor the pressure drop in the EC until the pressure in the EC has stabilized. Record P2.
9. Repeat the steps above to carry out the next set of solubility experiment.

Shut Down Procedure

1. Switch off the magnetic stirrer at EC.
2. Reduce the temperature set point at thermostat heating bath to room temperature.
3. Perform purging steps for EC and MV
4. Once the bath temperature has dropped to below 50°C, close Valve V-13 and V-14.
5. Stop the bath circulation and switch it off.
6. Switch off control panel
7. Return all valves to initial position.

Density Experiment Laboratory Manual

1. Prepare the aqueous amine of DEA + AHPD with difference concentration of (0 wt% DEA + 30 wt% AHPD), (10 wt% DEA + 20 wt% AHPD), (20 wt% DEA + 10 wt% AHPD) and (30 wt% DEA + 0 wt% AHPD).
2. Set the desired temperature at the monitor and create a file name to store the data.
3. Extract 5ml of solution using a syringe and slowly inject it into the densitometer through injection port. Make sure the tip of syringe is at dry condition.
4. Once the solution flows out from the outlet, stop injection. Press "Start" button.
5. Record the result after 45 minutes – 1 hour.
6. Inject the remaining solution into the densitometer. Then, inject water to wash out the solution by switch on the pump.
7. Repeat step 2 to 6 for difference concentration of solution.

Viscosity Experiment Laboratory Manual

1. Prepare the aqueous amine solution as per density experiment.
2. Plug a syringe filled with cleaning liquid (acetone) into capillary and rinse the capillary. Repeat for a few times until no traces of liquid are left.
3. Blow the capillary dry with the built-in air pump.
4. Drop the steel ball into the capillary and fill it with the aqueous amine solution.
5. Make sure no bubbles inside the capillary. Then, insert the capillary into the capillary block.
6. Enter the desired temperature and hit "Start" for Lovis to start measure.
7. Repeat step 2 to 6 for temperature at 303 K till 333 K and difference concentration of aqueous amine solution.